

# **Infrared Optical Constants of Particles in the Lower Stratosphere and Upper Troposphere**

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## **Progress Report for work performed 2-1-99 through 6-1-99 on Project #NAG5-8127**

### **Introduction**

This project deals with laboratory measurements of the infrared optical constants of various aerosol species at compositions and temperatures relevant to the upper troposphere and lower stratosphere. In particular, the aerosol systems of interest are: water ice, sulfuric acid/water, nitric acid/water, ternary mixtures of sulfuric acid/nitric acid/water and ammoniated sulfates.

Work is currently underway to measure the infrared optical constants of water ice in the near infrared. While the infrared optical constants of ice are fairly well determined in the mid IR, the currently available measurements in the near IR show a considerable amount of disagreement [Warren,1984]. Hence we are extending our previous studies to include thicker ice films so that the near infrared optical constants can be better determined. The optical constants are determined by measuring the transmission of infrared light through ice films of varying thickness over a frequency range from about 500 to about 7000  $\text{cm}^{-1}$ . Preliminary results are presented below.

### **Experimental**

The apparatus used to measure the infrared spectra has been described in detail previously [Tisdale et al., 1997]. Briefly, ice films were formed by condensing water vapor onto a cold 50 mm diameter silicon wafer mounted in a vacuum chamber and cooled by a liquid nitrogen cryostat. An ice film thickness of about 45  $\mu\text{m}$  was achieved after condensation for  $\sim 2$  hrs. The vapor was dosed onto the surface directly to form predominantly single-sided films of ice on the silicon wafer. The temperature of the silicon wafer was measured with type T thermocouples. The thermocouple junctions were attached to a copper heating plate in close thermal contact with the silicon. Experiments have thus far been performed for ice films at temperatures of 150, 160, 170 and 180 K. The infrared absorbances of the films were measured in transmission using collimated light from a Nicolet Magna 550 FTIR spectrometer at 4  $\text{cm}^{-1}$  resolution with 12 scans co-added.

In our experimental geometry, incident infrared light normal to the surface undergoes multiple reflections within the substrate as well as between and within the thin films [Toon

et al., 1994]. The theory used to extract the optical constants from the measured infrared spectra obtained with this geometry has been described in detail previously [Toon et al., 1994] and will only be discussed briefly. Equations have been developed to calculate the transmission of light through the thin film system [Toon et al., 1994]. The model assumes the presence of a slight film on the rear side of the wafer. Because of the direct dosing technique we expect very few molecules to stick to the rear side, and based on the amplitude of the observed interference fringes, we estimate the thickness of the film on the back side to be only about 1% of that on the top. The determination of the optical constants is an iterative process with two steps that are repeated until a converging solution is reached. In the first step the thickness and coherence of the films are calculated by minimizing the squared difference between the calculated and measured absorbances of the infrared spectra. The first time through the iterative loop, estimated refractive indices [from Toon et al., 1994] are used to calculate the thickness and coherence. In the subsequent iterations the newly calculated refractive indices are used. In the second step the refractive indices are adjusted as follows: the imaginary index at each frequency is determined to minimize the squared error between the calculated and measured spectra for all the chosen films simultaneously. Then the values of the real index at each frequency are calculated using the Kramers-Kronig relationship.

### **Work Currently in Progress:**

Work is underway to fit the infrared spectral data of water ice films at 150, 160, 170 and 180 K to extract the optical constants at the respective temperatures using the method described above. A typical fit between the measured and calculated absorbance that we are currently able to achieve is shown in Figure 1. The imaginary refractive indices extracted from the absorbance data and the method described above as a function of frequency are plotted in Figure 2 for 150, 160 and 170 K.

In the case of the thicker ice films we have found it to be difficult to pick out clear interference fringes for the purpose of estimating film thickness. The primary reason for this difficulty is the absence of a frequency window that is completely devoid of absorption bands. In particular, weak absorption bands centered around  $5000\text{ cm}^{-1}$  and  $6690\text{ cm}^{-1}$  become enhanced in intensity for the thicker films. Growing thick films is crucial for the determination of the optical constants in the near- and far infrared regions, where absorption features are weak. We are thus exploring alternative ways to estimate the thickness of these thick films. In particular, an attempt has been made to relate the calculated absorbances of chosen peaks (based on the model of the thin films) to the actual film thickness, and these estimates of the thicknesses have been successfully used as initial guesses in the method described above to extract the optical constants.

A comparison of our preliminary near IR optical constants at 170 K to those of earlier studies is shown in Figure 3. Also shown is our estimate of the minimum value of  $k$  ( $k_{\min}$ ) we can determine for films  $45\text{ }\mu\text{m}$  thick. It can be seen that our data at 170 K agrees reasonably well with the studies of Gosse et al. [1995] and Kou et al. [1993] at temperatures near 250 K. However there are significant differences in peak positions in

several cases. Our immediate priority is to make measurements on thicker films so that we can better determine the low  $k$ 's in the near IR. We will then extend our temperature range to determine if the observed differences in the data sets are due to temperature-dependent refractive indices.

### Future Work on Water Ice:

We also plan to extend the measurement of the optical constants of water ice to warmer temperatures of at least 230 K and warmer if experimentally feasible. There is a significant amount of thermal radiation in the earth's atmosphere beyond a wavelength of 20  $\mu\text{m}$ , but few data are available on the optical constants of ice in the far IR. Experiments will be performed as a function of temperature since the temperature sensitivity in the far IR is expected to be large [Warren, 1984].

### Other Systems:

It is also proposed to measure the optical constants of  $\text{HNO}_3/\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  ternary mixtures and ammoniated sulfates covering the entire range of compositions and temperatures that prevail in the upper troposphere and lower stratosphere. In the case of the  $\text{HNO}_3/\text{H}_2\text{O}$  system, recent balloon-borne particle analysis experiments [Schreiner et al., 1999] imply  $\text{H}_2\text{O}:\text{HNO}_3$  molar ratios of  $>10$  at atmospheric temperatures between 189-192 K. This value of the molar ratio is much higher than was previously considered. We plan to measure the infrared optical constants of such dilute  $\text{HNO}_3/\text{H}_2\text{O}$  mixtures as suggested above. An interpolation scheme will then be developed to provide optical constants for compositions that may not have been measured. The discrepancies that exist between the optical constants measured using different techniques will also be analyzed.

### References:

1. Owen B. Toon, Margaret A. Tolbert, Birgit G. Koehler, Ann M. Middlebrook and Joseph Jordan, *Infrared optical constants of water ice, amorphous nitric acid solutions, and nitric acid hydrates*, J. Geophys. Res. **99** 25631-25654 (1994).
2. Robert T. Tisdale, David L. Glandorf, Margaret A. Tolbert and Owen B. Toon, *Infrared optical constants of low-temperature  $\text{H}_2\text{SO}_4$  solutions representative of stratospheric sulfate aerosols*, J. Geophys. Res. **103** 25353-25370 (1998).
3. S. G. Warren, *Optical constants of ice from the ultraviolet to the microwave*, Appl. Optics, **23** 1206-1225 (1984).
4. L. Kou, D. Labrie and P. Chylek, *Refractive indices of water and ice in the 0.65 to 2.5  $\mu\text{m}$  spectral range*, Appl. Optics, **32** 3531-3540 (1993).
5. S. Gosse, D. Labrie and P. Chylek, *Refractive index of ice in the 1.4-7.8  $\mu\text{m}$  spectral range*, Appl. Optics, **34** 6582-6586 (1995).
6. J. E. Bertie, H. J. Labbe and E. Whalley, *Absorptivity of ice I in the range 4000-30  $\text{cm}^{-1}$* , J. Chem. Phys. **50** 4501-4520 (1969).

7. J. Schreiner, C. Voigt, A. Kohlmann, F. Arnold, K. Mauersberger and N. Larsen, *Chemical analysis of polar stratospheric cloud particles*, Science, **283** 968-970 (1999).

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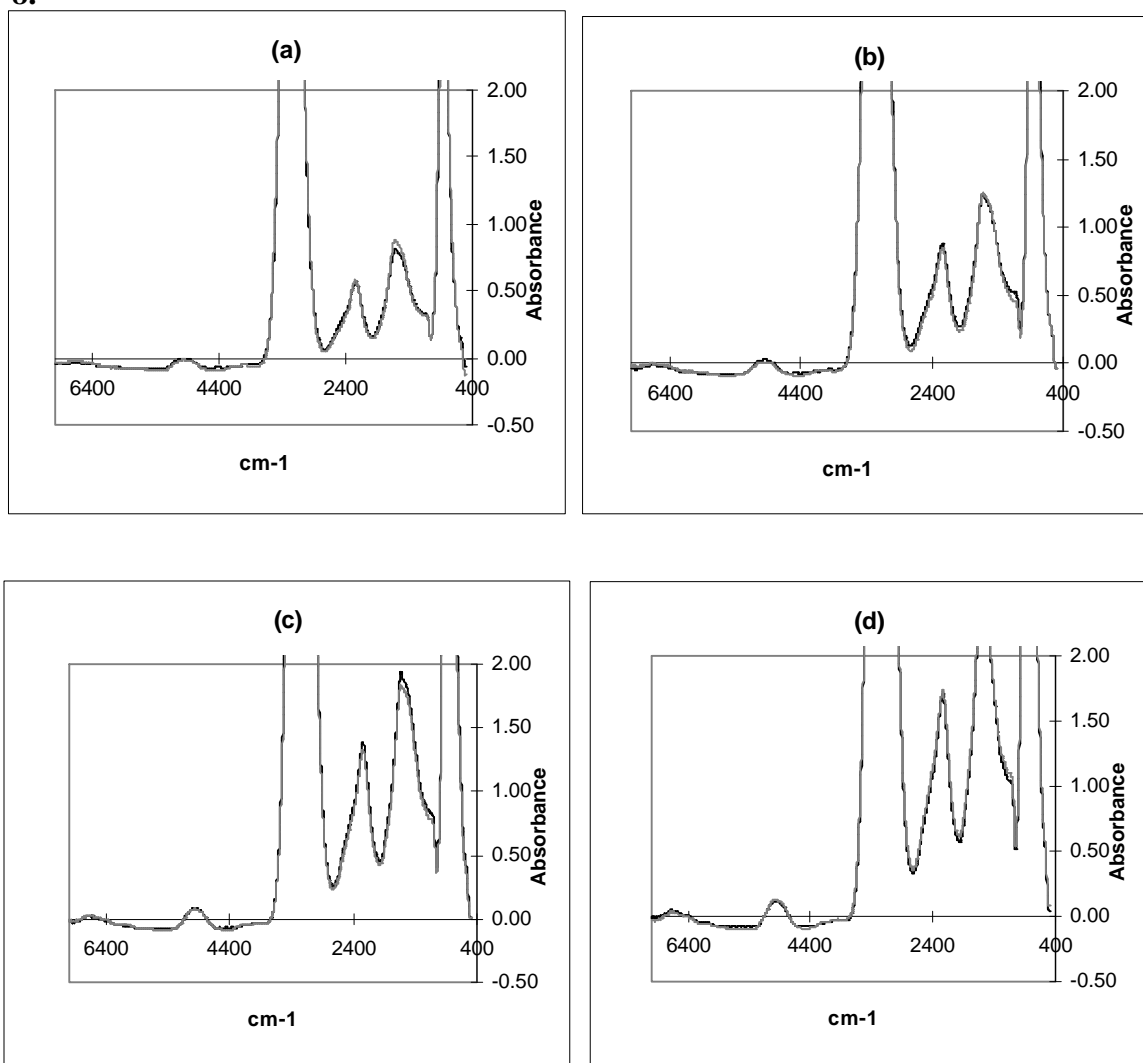


Figure 1: Measured (grey) and calculated (black) absorbances for the following thicknesses at 170 K: (a) 16.1  $\mu\text{m}$ , (b) 23.8  $\mu\text{m}$ , (c) 36.3  $\mu\text{m}$  and (d) 44.5  $\mu\text{m}$ .

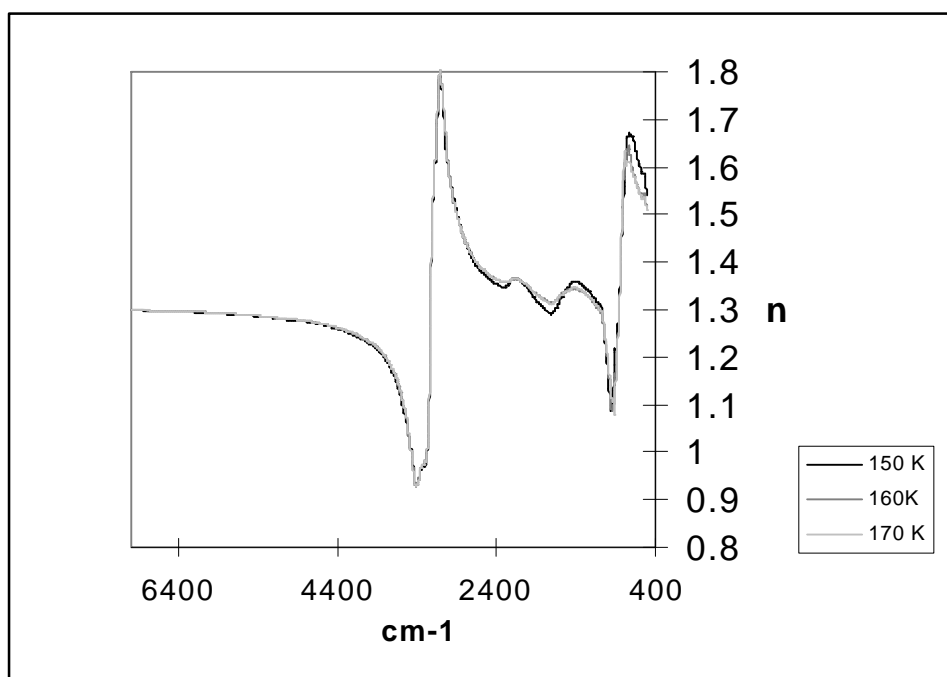
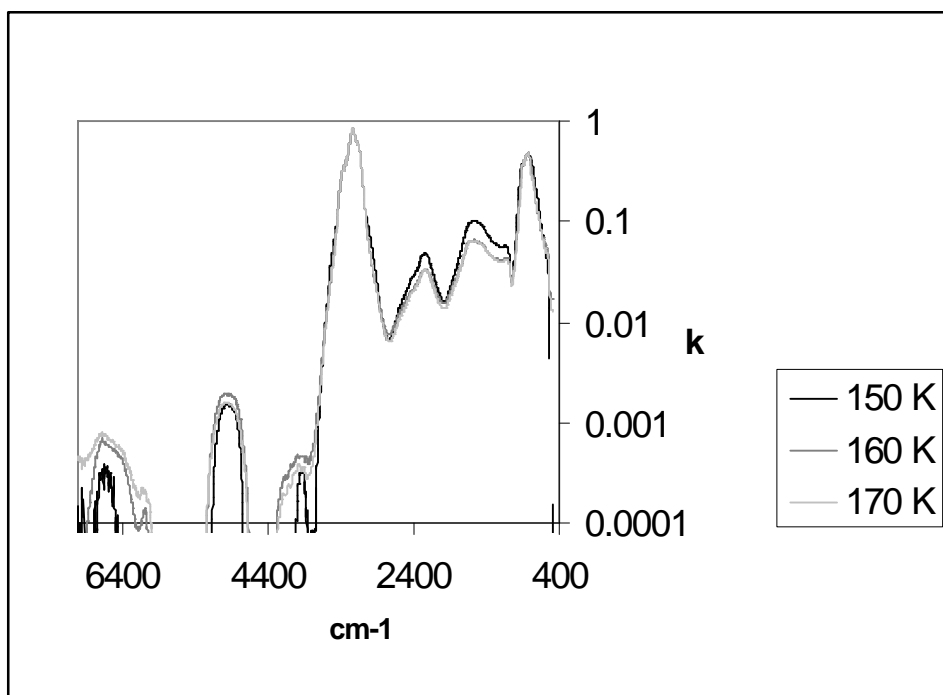


Figure 2: The imaginary index,  $k$ , and the real index of refraction,  $n$ , as a function of frequency at 150, 160 and 170 K.

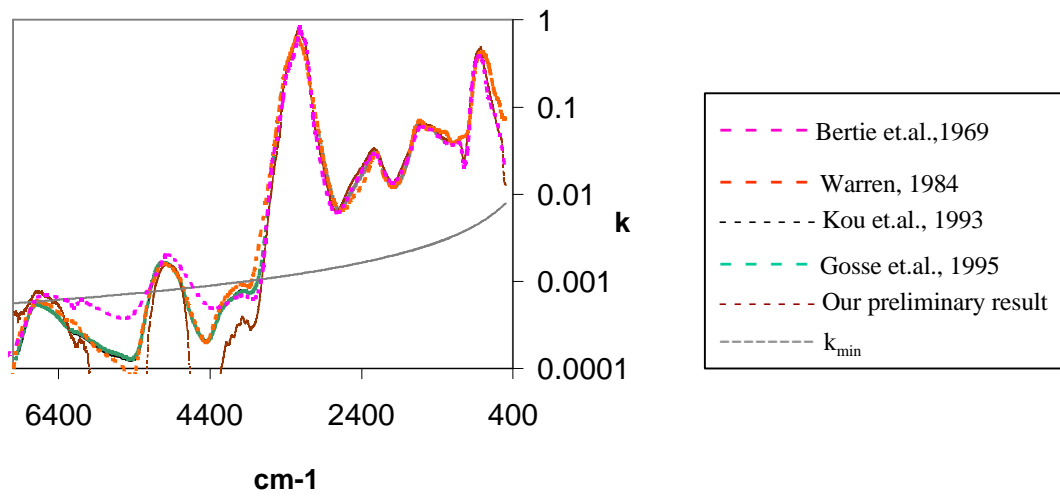


Figure 3: Comparison of the imaginary index of refraction,  $k$ , with previous work. The curve  $k_{\min}$  represents our estimate of the smallest value of  $k$  that could be measured accurately for a film thickness of about 45  $\mu\text{m}$ .

